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Simulation of Self-Reproducing Micelles using a Lattice-Gas Automaton

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We simulate self-reproducing micellar systems using a recently introduced lattice-gas automaton[1]. This dynamical model correctly describes the equilibrium and non-equilibrium properties of mixtures of oil, water and surfactants. The simulations reported here mimic the experiments of Luisi *et al.*[2] in which caprylate micelles are formed by alkaline hydrolysis of immiscible ethyl caprylate ester. As in the laboratory experiments, we find an extended induction period during which the concentration of micelles remains small; thereafter the ester is consumed very rapidly with concomitant production of micelles.

I. INTRODUCTION

This article reports on simulations of autopoietic self-reproducing micellar systems that we have carried out using our recently introduced lattice-gas model for self-assembling amphiphilic systems[1]. A self-reproducing system is one in which the process leading to population growth, here of amphiphile and micelles, occurs as a result of the parent structures themselves. Additionally, a structure which is self-bounded and is able to self-generate due to reactions which take place at or within that boundary, meets the criteria of *autopoiesis*, which certain authors have advocated as a minimal definition of life[3,4].

Our model simulates the behavior of various experimental systems that have been investigated in recent years. Experiments on micelles that can catalyse their own reproduction were first described in and around 1990-1991[5-7]. In these, micelles were present in the initial reaction mixture – that is, the system was presented with the bounded structures required for autocatalysis. Then in 1992 Bachmann, Luisi and Lang[2] reported on a two-phase system in which autocatalytic micelles were formed from amphiphiles that were themselves generated from a hydrolysis reaction within the aqueous solution. The system contained an aqueous sodium hydroxide solution and an ester, ethyl caprylate, which is itself immiscible with water. During the reaction, the system is well stirred in order to enhance the mixing of the two liquids. Hydrolysis of the ester initially produces the amphiphile monomer, sodium caprylate, which is known to form micelles in water[8]. This process occurs at a "slow" background reaction rate, largely confined to the ester-water interface. However, as soon as sufficient caprylate is present in the system for aggregation into micelles to take place (which occurs at and beyond the critical micelle concentration, in the terminology of equilibrium thermodynamics), a sudden increase in the reaction rate is observed. Bachmann *et al.* interpreted this as being due to a micellar catalytic process: When a micelle is formed, its hydrophobic interior causes it to rapidly bind oily ethyl caprylate molecules, dramatically enhancing the solubility of the previously immiscible liquid. The rate of hydrolysis is suddenly increased because the ester is now dispersed throughout the aqueous medium and its probability of encountering water-soluble hydroxide ions is vastly greater. Moreover, new amphiphile is produced by a chemical reaction that takes place at or within the domain boundary of the

parent micelles, thereby qualifying as an instance of autopoietic self-reproduction. This amphiphile is then able to form more micelles, and the hydrolysis reaction accelerates. The latter reaction process is the "fast" micellar catalysis step, the rate of micelle production increasing as the micelle concentration increases. The reaction is completed when there is no longer any ethyl caprylate left in the system. Upon lowering the pH of the system, Bachmann *et al.* found that the product micelles could be reversibly converted into vesicles formed from closed caprylate bilayer membranes. These authors argued that the properties of such systems may have relevance to chemical mechanisms associated with the origins of life on Earth[2].

In outline, the physicochemical steps occurring can be written down as rate processes:

$$
\begin{aligned}
EC &\to C, \\
nC &\to C_n, \\
C_n + EC &\to C_n + C.
\end{aligned}
\tag{I.1}
$$

where EC denotes ethyl caprylate, C the caprylate anion and C_n a caprylate micelle (n being the number of caprylate monomers per micelle, estimated[2] to be approximately 63). The third step here represents the micellar-catalysed hydrolysis of ester.

Although the qualitative explanation of the Luisi experiments proffered here is simple enough to comprehend, producing a quantitative model of the phenomenon is quite a different matter. The difficulties stem from the need to describe the dynamics of micelle formation correctly. Only recently has a detailed nonlinear dynamical model of micelle formation kinetics been proposed and analysed[9], with particular reference to Luisi's system (see also[10]). The approach is based on a generalisation of the Becker-Döring scheme describing the kinetics of first-order phase transitions[11], in which micellar clusters grow (shrink) through the stepwise addition (removal) of individual surfactant monomers. The general kinetic process in the Becker-Döring theory can be written as

$$
C_r + C \underset{}{\overset{a_r, b_{r+1}}{\rightleftharpoons}} C_{r+1},
\tag{I.2}
$$
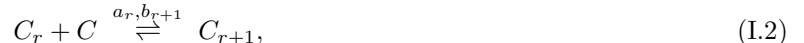
where C_r is a cluster comprising r monomers and r ranges from one to infinity. Here a_r and b_{r+1} are the rate coefficients for the forward and reverse steps respectively. The reaction rates are given by the law of mass action, and lead to an infinite system of coupled nonlinear differential equations which may be combined with the processes shown in the scheme (I.1)[9].

At a more microscopic level, one would like to be able to describe micellar dynamics accurately. This is one aspect of the wider issue of the challenge of modelling self-assembling amphiphilic systems. Although in principle one might wish to use molecular dynamics to simulate the interactions in these systems in full molecular detail, in practice such an approach is computationally overbearing and will remain so for the foreseeable future given the state of today's technology. Moreover, some of the most important situations demanding attention involve the coupling of self-assembly with hydrodynamics[12]. Their complexity is the result of the interplay between microscopic interactions and mesoscale hydrodynamic effects. Accordingly, we have developed a lattice-gas model of such systems which is capable of addressing these issues in a computationally tractable manner.

The purpose of the present paper is to show how our model may be applied to simulate the dynamics of self-replicating micelles. Even at equilibrium, such structures are highly dynamic, rapidly exchanging monomers with the surrounding medium on timescales which are typically of the order of micro- to nanoseconds. This makes these processes very difficult to capture using molecular dynamics (MD), where the integration time-steps are on the order of femtoseconds. By contrast, lattice gas automata are based on a discrete time-stepping procedure performed on a spatially discrete lattice: The interactions are confined to collisions at the vertices, and the particles are then advected to neighboring sites in time steps that are on the order of the mean free time, several orders of magnitude larger than those in MD.

The formation of micelles from surfactant monomers is an important part of the simulations described here. In addition, however, in the self-reproducing micelle experiments a chemical reaction is involved which converts the oily ester into surfactant molecules. Again, it is a strength of cellular automata that they enable chemical reactions to be included easily by means of simple collisional transition rules; examples include the Belousov-Zhabotinski reaction[13], the Schlögl model[14], and cement hydration[15]. We shall find

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that our suitably modified lattice-gas automaton model displays the same behaviour as that shown in the real system of self-reproducing micelles. It therefore bridges the divide between the two approaches to the investigation of autopoietic structures advocated by Varela[16]: virtual (computational) and physical (chemical synthesis). Cellular automata were originally proposed as providing a virtual model of autopoiesis by Varela *et al.*[3]; it is therefore fitting that we are able to connect the logical and the physical through a finite-state automaton simulation of the physical approach. Indeed, we hope that our results may be seen as being of wider significance than purely as simulations of phenomena in the natural world. For in recent years, there has been a renewed interest in the concept of "artificial life," the study of life as it could be (in whatever shape or form it may be found or made on Earth or elsewhere), rather than as it is known today on Earth[17]. According to this view, neither actual nor possible life is determined by the matter of which it is composed. For life is a *process*, and it is the *form* of this process, not the matter, that is the essence of life. As von Neumann originally sought to demonstrate, one can ignore the physical medium and concentrate on the *logic* governing this process[18]. In principle, one can thus achieve the same logic in another clothing, totally distinct from the carbon-based form of life we know.

II. DESCRIPTION OF THE MODEL

Our lattice-gas model is a microscopic dynamical system which gives the correct mesoscopic and macroscopic behaviour of mixtures of oil, water and surfactant. The model is based on the two-fluid immiscible lattice gas of Rothman and Keller[19], which we have reformulated using a microscopic particulate decription to permit the inclusion of amphiphile. The model exhibits the commonly formed equilibrium microemulsion phases, including droplets, bicontinua and lamellae[1]. Moreover, the model conserves momentum as well as the masses of the various species, and correctly simulates the fluid dynamical and scaling behaviour during self-assembly of these phases[20,21].

In order to incorporate the most general form of interaction energy (Hamiltonian) within our model system, we introduce a set of coupling constants $\alpha, \mu, \epsilon, \zeta$, in terms of which the total interaction energy can be written as[1]

$$\Delta H_{\mathrm{int}} = \alpha \Delta H_{\mathrm{cc}} + \mu \Delta H_{\mathrm{cd}} + \epsilon \Delta H_{\mathrm{dc}} + \zeta \Delta H_{\mathrm{dd}}. \tag{II.3}$$

The four terms on the right hand side correspond, respectively, to the relative immiscibility of oil and water, the tendency of surrounding surfactant to bend around oil or water droplets, the propensity of surfactant dipoles to align across oil-water interfaces and the contribution from pairwise interactions between surfactant molecules.

In the experiments of Bachmann *et al.*[2], the caprylate amphiphile produced has a tendency to form micelles in the bulk water phase rather than predominantly congregating in monolayers at the oil-water interface. Previous studies with our model[1] enable us to simulate this property by choosing the following set of coupling constants:

$$\alpha = 1.0, \mu = 1.0, \epsilon = 3.0, \zeta = 0.5, \tag{II.4}$$

for our simulations. There is another parameter present in our model that must be specified, called β. This coefficient arises from the stochastic, Monte-Carlo-like, nature of the selection of outgoing collisional states at vertices within our lattice-gas automaton, and can be thought of as an effective inverse temperature-like parameter[21].

From the discussion of Luisi's self-reproducing micelle experiments given in Sec. I, it is clear that the autocatalytic nature of the reaction is related to the critical micelle concentration (c.m.c.) of the caprylate anion. Experimentally, this is the point when the *equilibrium* concentration of surfactant monomers reaches a level at which they associate into micelles. However, it is important to recognise that the c.m.c. is not the location of a sharp phase transition, but rather the concentration at which the equilibrium fraction of monomers in micelles reaches some arbitrary value, usually taken to be 0.5. Indeed, the equilibrium fraction of monomers within micelles is itself somewhat arbitrary, since there is no clear-cut division between "micelles" and smaller (or, for that matter, larger) clusters that are not regarded as micelles. The equilibrium

fraction of monomers in micelles varies very rapidly with monomer concentration around the c.m.c., so that to an experimentalist it may look like a phase transition. As in our work based on the generalised Becker-Döring equations[9], our lattice-gas model dispenses completely with the commonly made assumption of thermodynamic equilibrium between monomers and monodisperse micelles, being a highly dynamical, nonequilibrium model. Thus, we do not assume the existence of a critical micelle concentration: Rather, the phenomenon is itself an emergent property of our model.

At the mesoscopic level, our model is very useful for analysing the kinetics of micellar growth. Indeed our model has already been shown to exhibit a critical micelle concentration in the binary – surfactant and water (or oil) – limit[1]. Using the set of coupling constants as defined in Eq. II.4, we reproduce this analysis in order to obtain an estimate for the number of surfactant particles required to be in the binary water-surfactant system for the c.m.c. to be exceeded. The results can be found in Sec. III.

Although an extension of our full microemulsion model to three dimensions is currently underway[22], in this letter we shall be concerned only with the two-dimensional ($2D$) version. This is sufficient to capture the salient properties of the micellar self-production experiments; we expect the results in the $3D$ case to be qualitatively similar.

In the basic simulation (as in the experiments) the system is initially comprised of two immiscible fluids: The majority phase we identify with the aqueous solution in the experimental set-up; the other, minority, phase we take to be representative of the ethyl caprylate ester. We then specify two chemical reaction mechanisms designed to represent: (i) the "slow" pseudo-first-order alkaline hydrolysis of caprylate by hydroxide ions present within the aqueous medium producing surfactant, and (ii) the "fast" micellar-catalysed hydrolysis during which self-assembled micelles greatly enhance the solubility of ester within the water phase and thus lead to an increased alkaline hydrolysis. As in the actual experiments, the simulation reaches completion once all the ester in the system has been hydrolysed.

Within our lattice-gas automaton, alkaline hydrolysis is described algorithmically by the conversion of an ester (oil) particle into an amphiphile particle if certain prescribed conditions are met; the system is otherwise allowed to evolve in the normal way (that is, with collisions conserving momenta and particle masses) and a record is kept of both the total number of surfactant particles in the system and the total number of micelles. (The precise manner in which "micelles" are defined in these simulations is specified below.) These data can then be used to analyse our simulations in a manner similar to that used for the experimental data generated by Bachmann *et al.*[2].

In order to simulate the self-reproduction of micelles, we set up the model as follows:

1. The $2D$ simulation domain with periodic boundary conditions in both dimensions is initialised with water and oil in a 6 : 4 ratio, the two bulk fluid regions being entirely phase-separated in accord with the experimental starting conditions.

2. The inverse-temperature parameter β was set to the value 0.137. This value corresponds to the oil and water acting as immiscible fluids during the simulation (that is, below the so-called spinodal point at which the fluids become miscible), but where the natural fluctuations within the system (which are larger near the spinodal point) encourage invasion of the individual bulk, phase-separated fluid regions by particles of the opposite kind. This has a similar effect to continuous stirring in the experimental system, since both enhance the ester hydrolysis rate, in essence by increasing the interfacial area.

3. At each timestep and for every site $\mathbf{x}$ on the lattice which contains *at least one oil* particle, we perform the following analysis

   - "Slow" (pseudo-first-order) hydrolysis step: If five of the six nearest-neighbor sites are dominated by water particles, and less than two of these nearest-neighbor sites have amphiphile present (recall that there can be up to seven particles per site), then one of the oil particles on site $\mathbf{x}$ is converted into a surfactant particle with unit probability, prior to determining the outgoing state of the collision process from the look-up tables. This simulates ester hydrolysis in an overwhelmingly aqueous environment.

   - "Fast" micellar catalysis step: If five or more of the six nearest-neighbor sites contain one or more surfactant particles and five or more of the six next-nearest-neighbor sites have water particles

present, we define this structure as being equivalent to a micelle*. Within this bounded structure a surfactant particle is created from an oil particle on site **x** with probability one, prior to determining the outgoing state of the collision process from the look-up tables. If there is more than one oil particle at site **x** then the oil particle actually converted is chosen at random; this prevents any bias from developing in the velocity given to the newly created surfactant particles. Chemically speaking, this step simulates the hydrolysis of an ester molecule solubilised within a micelle, by hydroxide ions in the surrounding aqueous environment.

- Otherwise the automaton is updated according to the usual collision rules[1].

4. We keep track of the total number of surfactant particles present in the system as well as the number of micelles (as defined above) existing at each time step. Note that in addition to these "oil-in-water" type micelles, we also need to take into account similar nearest- and next-nearest-neighbor structures for which the central site is surfactant dominated. Otherwise the number of micelles present in the system would appear to drop to zero once all the oil in our system is converted to amphiphile.

III. SIMULATION RESULTS

Initially we report on the analysis of the c.m.c. in a binary water-surfactant limit of our model. Simulations are on a 64×64 lattice with the initial condition being a random distribution of the water and surfactant particles; the density of surfactant in the system is altered in each case. When sufficient amphiphile is present for the monomers to form micelles, these impart characteristic structure to the system which should be discernible in our simulations. To perform a quantitative analysis we keep track of the circularly-averaged structure functions $S(k, t)$ of the surfactant density[1]. The micelles themselves are dynamic structures and are not necessarily very long lived; in addition energetic considerations mean that individual micelles do not grow without limit, hence we do not expect to see evidence of micelles coalescing and growing in an unbounded manner. The results of our simulations are shown in Figs. 1 and 2.

From Fig. 1 it is clear that for a reduced density of 0.01 surfactant (≈ 287 surfactant particles) there is no structure formation during the timescale of the run, so the amphiphile exists as monomers. In contrast, for 0.03 surfactant (≈ 860 surfactant particles) the figure shows structure formation early in the simulation which is maintained and does not appear to grow without limit, indicating that we have just reached the c.m.c. To further clarify the approximate position of the c.m.c., Fig. 2 shows the results for reduced densities of 0.02 (≈ 573 surfactant particles) and 0.04 (≈ 1147 surfactant particles) surfactant. The former of these is below and the latter above the c.m.c. for this system. These results indicate that the number of surfactant particles required to be in the system for the c.m.c. to be exceeded lies between 573 and 860.

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[0]*Note that in reality there are *twelve* next-nearest-neighbor sites on a hexagonal lattice. The six we specify here are those that lie along the directions defined by the six nearest-neighbor lattice directions from site **x**: This defines points around an essentially circular structure (which would be spherical in 3D), is computationally simple to implement and suffices for our present purposes.
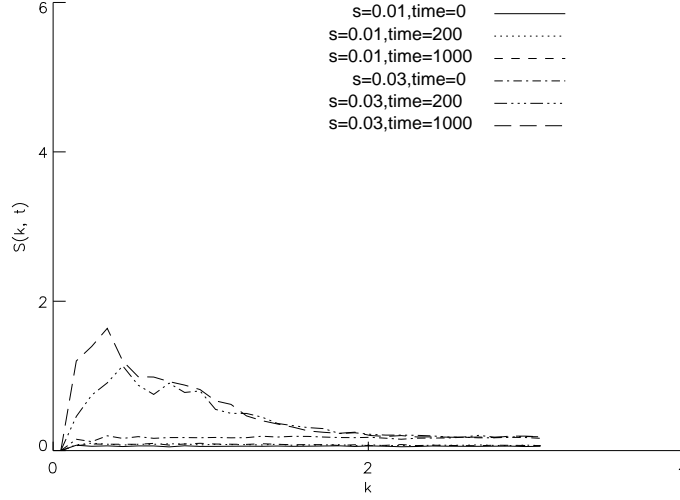
FIG. 1. Temporal evolution of surfactant density structure function S(k, t) for binary water and surfactant mixtures. The figure contains results for both 0.01 and 0.03 reduced density of surfactant.
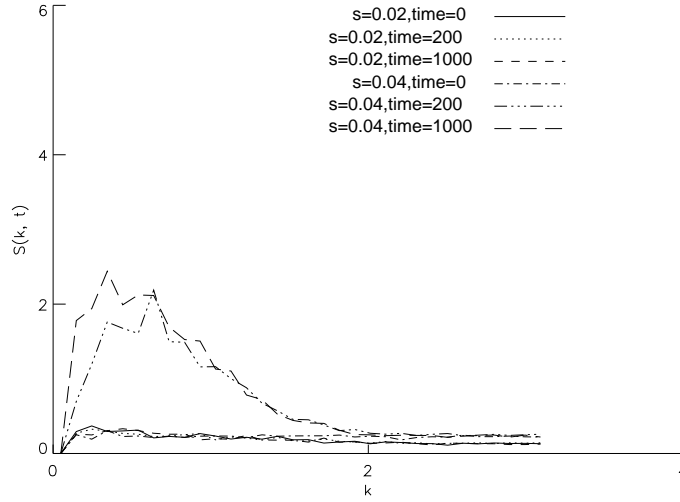

FIG. 2. Temporal evolution of surfactant density structure function S(k, t) for binary water and surfactant mixtures. The figure contains results for both 0.02 and 0.04 reduced density of surfactant.

The result of a typical simulation of self-reproducing micelles using the lattice-gas model described in Sec. II is shown in Fig. 3. The plot consists of the temporal evolution (in dimensionless lattice-gas automaton time steps) of the number of surfactant particles in the system as well as the number of micelles on a lattice of size 64×64. The comparison with the experimental results of Bachmann *et al.* is good: We see a relatively long initial induction period during which surfactant particles are produced by the "slow," pseudo-first-order hydrolysis step only; this is followed by an extremely rapid increase in the number of surfactant particles in the system which occurs at exactly the point at which micelles start to form. For, in accord with the estimate given above for the binary system, the amphiphile concentration at this point ($\approx 600 - 700$ surfactant particles on the lattice) is at the critical micelle concentration. Figure 4 shows a sequence of snap-shots from the above described simulation at three different moments during the simulation: (a) shows

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the situation shortly after the initial time, when fluctuations have caused particles from the immiscible fluids to interpenetrate; (b) depicts the mixture at the onset of the rapid phase in the reaction as amphiphile begins to be generated freely; and (c) displays the homogeneous end state of the reaction, where all the oil (ester) has been converted into amphiphile.
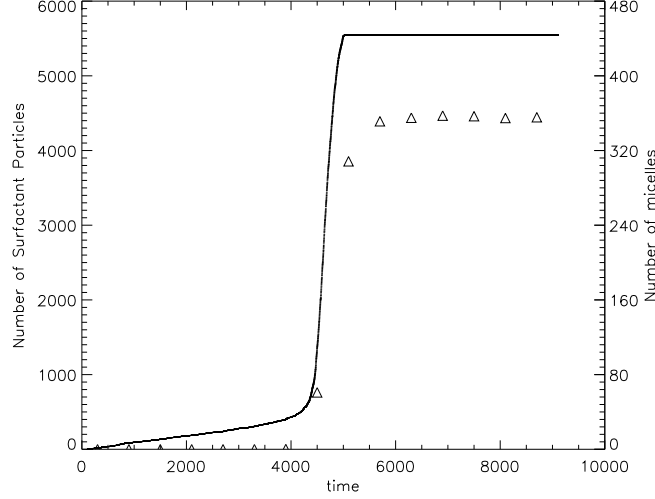

FIG. 3. Amphiphile and micelle concentration as a function of time step in the lattice-gas automaton model. The triangles are for the micelles and correspond to the values indicated on the right hand vertical axis.

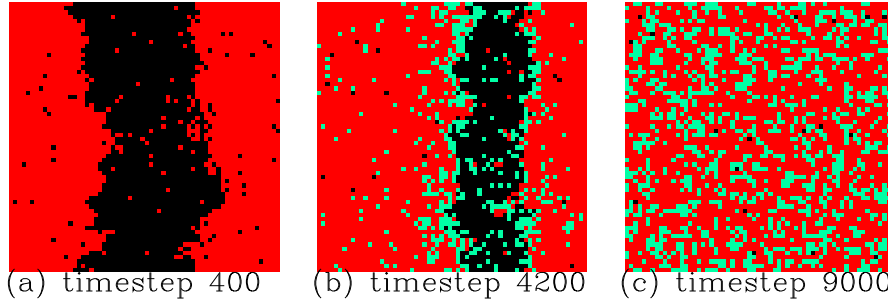(a) timestep 400   (b) timestep 4200   (c) timestep 9000

FIG. 4. Three snapshots in time from the evolution of the lattice-gas automaton simulation. Ethyl caprylate molecules are black, water is red and anionic caprylate is green.

Fig. 5 contains the result for an exactly analogous simulation to that described above but now the system is given a non-zero initial surfactant concentration. We use a reduced density of 0.005 which corresponds to about 150 surfactant particles randomly spread around the 64×64 lattice. The presence of these particles should induce an earlier onset of the rapid growth phase since the system should reach its critical micelle concentration more quickly. In accord with the experimental results of Bachmann et al.[2], this is exactly the behavior that we observe.
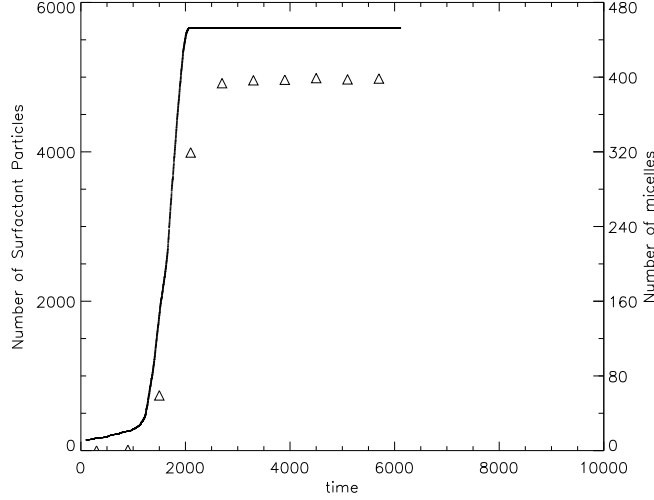
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FIG. 5. Amphiphile and micelle concentration as a function of time step in the lattice-gas automaton model. The triangles are for the micelles and correspond to values on the right hand vertical axis. This case has surfactant in the system at time zero.

Note that in Fig. 5, the calculation of the number of micelles present at each timestep is done with approximately 150 extra surfactant particles in the system than is the case for Fig. 3. This accounts for the perceived discrepancy in the number of micelles found in solution after the reaction has completed in each case. The system shown in Fig. 5 is found to have a slightly higher number of micelles because of the extra amphiphile monomers initially present in the solution. Again, by looking for the end of the "slow" hydrolysis step, we can estimate the critical micelle concentration for this system; as expected it is found to be approximately the same as in the previous simulation and so is also in agreement with the prediction from the binary water-surfactant mixture.

It must be remembered that these lattice-gas simulations are of a microscopic, particulate nature, in contradistinction with our nonlinear dynamical models[9]. They are therefore subject to statistical fluctuations. Accordingly, we have also performed a series of simulations on progressively larger 2D lattices (64×64, 128×128 and 256×256) in order to investigate the role of these fluctuations. At the same time, we have ensured that, in all cases, the simulations start from the *same* interfacial area to volume ratio for the oily ester (in 2D, this is more correctly stated as the interfacial length to area ratio), as this is recognised to be an important parameter in the experimental set-up[2]. (Experimentally, more rapid stirring leads to an enhanced ester/aqueous-phase interfacial area and hence a faster overall rate of reaction.) We carried out five such simulations for each size of lattice, differing only in the precise specification of the initial condition – the distribution of initial particle velocities within the bulk regions at timestep zero is randomised with a different seed for each run, leading to different fluctuation effects in each case. The results are summarised in Table I, which lists statistics for the time taken for the "slow" induction period to come to an end and so also marks the point at which the rapid reaction phase begins.

TABLE I. **Effect of lattice size on end of induction phase in lattice-gas automaton simulations of Luisi's experiments**

Lattice size	Average timestep t_0 of "fast" phase	Standard deviation	Furthest deviation from t_0
64×64	3827	784.71	1193
128×128	3821	210.84	302
256×256	3835	144.52	221

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We find that the average timestep at which kick-off occurs is essentially constant across these simulations, while deviations from average behaviour are greatest for the smallest simulation box size and least for the largest. This is exactly what one would expect: As the number of particles in the system becomes larger, fluctuations are less significant and the average behavior (of an ensemble of similar systems) becomes ever closer to that observed experimentally.

IV. CONCLUSIONS

Using our recently introduced lattice-gas model which describes mixtures of surfactant, oil and water[1], we have been able to simulate the experimentally observed kinetics of Luisi's self-reproducing micelles[2]. In the simulations, a characteristic induction period is followed, at the onset of the model's critical micelle concentration, by a very rapid production of surfactant and micelles. The induction period is shortened by the initial addition of surfactant, and by increasing temperature (which can also be taken to correspond to higher stirring rates of the fluids inside the reaction vessel). The length of the induction period is also sensitive to fluctuations within the system; however, for ensembles of systems in which the interfacial area to volume ratio of the ester initially present is held constant, the ensemble average of the induction time is essentially independent of system size.

Our simulations bring out very clearly one essential element in the self-reproduction of caprylate micelles during the aqueous alkaline hydrolysis of ethyl caprylate. This is the highly *dynamic* nature of the entire process, including the reversible self-assembly and break-up of the micelles themselves, which are also central features of our previous Becker-Döring model[9]. Moreover, "micelles" generally persist as clusters of a range of sizes. The self-reproducing micelle experiment has been proposed as a paradigm of an autopoietic process[23], but it must be remembered that the micellar structures are themselves evanescent – they are continually breaking up and reforming. This is a property shared with living things, whose overall forms may remain largely invariant but whose detailed molecular constitutions are perpetually in a state of flux.

[1] Boghosian, B.M.; Coveney, P.V.; Emerton, A.N. "A Lattice Gas Model of Microemulsions" *Proc. Roy. Soc. London, Series A* (in press 1996).

[2] Bachmann, P.A.; Luisi, P.L.; Lang, J. *Nature* **1992**,*357*, 57-59.

[3] Varela, F., Maturana, H., Uribe, R. *Biosystems* **1974**, *5*, 187-196.

[4] Fleischaker, G.R., Colonna, S., P.L. Luisi (eds), *Self-Production of Supramolecular Structures* NATO ASI Series *446*; Kluwer: Dordrecht, 1994.

[5] Bachmann, P.A.; Walde, P.; Luisi, P.L.; Lang, J. *J. Am. Chem. Soc.* **1990**, *112*, 8200-8201.

[6] Bachmann, P.A.; Luisi, P.L.; Lang, J. *J. Chimia* **1991**, *45*, 103-106.

[7] Bachmann, P.A.; Walde, P.; Luisi, P.L.; Lang, J. *J. Am. Chem. Soc.* **1991**, *113*, 8127-8130.

[8] Fendler, J.H.; Fendler, E.J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975; pp 19-41.

[9] Coveney, P.V.; Wattis, J.D. "Analysis of a generalised Becker-Döring model of self-reproducing micelles," **1995** submitted to *Proc. R. Soc. London, Series A*

[10] Billingham, J.; Coveney, P.V. *J. Chem. Soc. Faraday Transactions* **1994**, *90*, 1953-1959.

[11] Becker, R.; Döring, W., *Annal. Phys.* **1935**, *24*, 719-752.

[12] Jha, B.K.; Manna, S.N.; Shintre, S.N.; Kulkarni, B.D. *Colloids and Surfaces A: Phys. Eng.* **1996**, *108*, 73-81.

[13] Markus, M.; Hess, B. *Nature* **1990**, *347*, 56-58.

[14] Boghosian, B.M.; Taylor, W. *J. Stat. Phys.* **1995**, *81*, 295-317.

[15] Bentz, D.P.; Coveney, P.V.; Garboczi, E.J.; Kleyn, M.F.; Stutzman, P.E. *Modelling Simul. Mater. Sci. Eng.* **1994**, *2*, 783-808.

[16] Varela, F.J. in *Self-Production of Supramolecular Structures* Fleischaker, G.R., Colonna, S., P.L. Luisi (eds), NATO ASI Series, *446*; Kluwer: Dordrecht, 1994); pp 23-31.

[17] Coveney, P.V.; Highfield, R.R. *Frontiers of Complexity*; Faber & Faber: London, 1995; Fawcett: New York, 1995.

[18] von Neumann, J., *Collected Works*; Pergamon Press: Oxford, 1963.

[19] Rothman, D.H.; Keller, J.M. *J. Stat. Phys.* **1988**, *52*, 1119-1127.

[20] Frisch, U.; Hasslacher, B.; Pomeau, Y. *Phys. Rev. Lett.* **1986**, *56*, 1505-1508.

[21] Emerton, A.N.; Coveney, P.V.; Boghosian, B.M. "Lattice-gas simulations of domain growth, saturation and self-assembly in immiscible fluids and microemulsions" **1996** submitted to *Phys. Rev. E.*

[22] Boghosian, B.M.; Coveney, P.V.; Emerton, A.N. in preparation (1996).

[23] Luisi, P.L.; Varela, F.J. *Origins of Life and Evolution of the Biosphere* **1989**, *19*, 633-643.